# Energy dispersion in graphene and carbon nanotubes and molecular encapsulation in nanotubes

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Density-functional calculations of electronic and vibrational dispersion energies for pristine graphite monolayer (graphene) and single-walled carbon nanotubes (SWCNTs) are presented. Optimized parameters for nonlocal norm-preserving pseudopotentials which replace the potential field due to core electrons are given. Comparison with observations, where available, is made. The effect of encapsulation of carbon nanotubes with an alkali-halide matrix is numerically investigated. The electronic band structure of encapsulated SWCNT is noticeably modified, as is its charge density, and hence its optical properties.

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# I. INTRODUCTION

Isolated single-walled carbon nanotubes are pristine and ordered systems for fundamental studies in reduced dimensions. Their extremely large aspect ratio renders them ideal candidates for studies of quantum phenomena in nanoscale composite electronic devices in low dimensions.<sup>1</sup> The electronic and vibrational energy structures of nanotubes exhibit quantized bands that arise from the confinement around the nanotube circumference. Zone-folding techniques<sup>2</sup> have proven immensely successful in providing physically relevant information on the nature of electronic and vibrational interactions in carbon nanotubes. Ultrasmall-radii singlewalled carbon nanotubes (SWCNTs) are being investigated candidates for application in high-temperature as superconductors.<sup>3,4</sup> What is mainly missing from this class of calculations is the rehybridization of orbitals<sup>5</sup> brought about by the tube curvature. Study of graphitic systems such as single layer and bilayer graphene are in vogue, as their electronic structures exhibit novel behavior resembling twodimensional (2D) gases of massive chiral and massless fermions.<sup>6</sup> One- and zero-dimensional quantum behaviors, Kondo effect,<sup>8</sup> and Luttinger-liquid behavior<sup>9</sup> are expected in encapsulated carbon nanotubes.

Electronic and optical properties of carbon nanotubes are amenable to external perturbations and hence can be manipulated. Increased conductivity has been reported in doping of nanotubes with potassium and bromine,<sup>10,11</sup> and, in turn, the modified conductivity of nanotubes affects their interaction with electrons and ions. Previously proposed<sup>12</sup> quantized electronic structures hovering around nanotubes, observed recently,<sup>13</sup> possess properties that are greatly affected by changes in the tube conductivity. Modifications of the electronic structure of nanotubes have been reported in experiments on inserting C<sub>60</sub> molecules<sup>14</sup> and in encapsulating with alkali halides (KI).<sup>15</sup> The process of encapsulation is preferred due to air stability of the encapsulated system for device-specific applications.

In this work, we present an exploration of the electronic and phonon dispersions in pristine graphene and SWCNT, and alkali-halide encapsulated SWCNT. Self-consistent density functional theory<sup>7,16</sup> (DFT) and tight-binding method<sup>17</sup> are superior alternatives for the calculation of electronic and phonon states and optical response in graphite and SWCNT. Tight-binding calculations are faster,<sup>18,19</sup> but because the interactions are due to nearest-neighbor coupling, their predictive power and accuracy are less robust compared with the *ab initio* DFT methods.

We implement a version of the self-consistent, so-called order- $N[\mathcal{O}(N)]$  DFT algorithm suitable for large systems, the SIESTA method,<sup>20</sup> whose computational economy scales linearly with the number of atoms. The core electrons are replaced in this algorithm by nonlocal norm-conserving pseudopotentials<sup>21</sup> (PPs) and the valence electrons are treated with a linear combination of multiple- $\zeta$  and polarized basis sets of localized atomic orbitals (LCAOs). The core, core-valence exchange, and correlation effects are handled in the generalized-gradient approximation (GGA).<sup>22</sup> The electronic and phonon dispersion energies and electronic density of states for graphene, (6,6) and (10,10) armchair, and (10,0)zigzag SWCNT are calculated with optimized PP parameters and compared with results obtained using published PP parameters. Our results are also compared with experimental data, where available. The electronic dispersion spectra and carbon bond density for potassium-iodide matrix encapsulated (10,10) SWCNT are calculated. The electronic band structure of SWCNT is modified in the presence of encapsulation.

The PP,  $V_l(r)$ , is in a semiclassical form that depends parametrically on the electron angular momentum l and is partitioned into a nonlocal form, proposed by Kleinman and Bylander,<sup>23</sup> and a local part. The optimization of the local PP, for smoothness, which is sometimes called the transferability criterion, is achieved by choosing appropriate core radiione for each angular momentum state-beyond which the *l*-dependent potential and the local part of the PP are exactly equal, meaning that the pseudo and all-electron (AE) valence eigenstates have the same energy and the same amplitude outside a chosen core cutoff radius. A PP with transferability conditions will reproduce the AE energy levels and wave functions in different atomic, molecular, and solid-state environments. We compare and analyze the applicability and use of our optimized PP parameters with that of previously published values,<sup>25</sup> which we dub the "developers" parameters. For certain atoms, such as the alkali metals and alkaline-earth atoms, some core states are included with the

TABLE I. Pseudopotential parameters in atomic units.

PP parameters	r <sub>s</sub>	$r_p$	$r_d$	$r_f$	r <sub>cc</sub>
Optimized	2.40	0.55	2.40	2.37	0.50
Developers'a	1.25	1.25	1.25	1.25	1.50
<sup>a</sup> Reference 25.					

valence states, forming what is known as the semicore states.<sup>24</sup>

It must be expressed that the generation of a workable PP depends critically on the suitable choice of functionals that will later be used in the calculation of quantized electronic and phonon energies. The required consistency implies that a proper form of the exchange and correlation functionals to the Kohn-Sham DFT is employed. The primary functionals are the local-density approximation<sup>16</sup> (LDA) and the GGA,<sup>22</sup> which favors electron-density inhomogeneities more than LDA. The next critical aspect of PP generation is the choice of a cutoff radius  $r_l$ , where the AE and PP wave functions match with at least a continuous first derivative. A good portion of our current effort has concentrated on surveying the available published data for the core cutoff radii for graphite and carbon nanotubes and optimizing these parameters for the DFT calculations.

# **II. COMPUTATIONAL DETAILS AND RESULTS**

The DFT calculations were performed using the SIESTA *ab initio* package<sup>20</sup> within the GGA as parametrized in Ref. 22. The PP parameters were optimized to yield conserved total all-electron energies and pseudo-wave-functions. We found it necessary to include the core correction in the PP generation to account for the nonlinearity in the exchange-correlation potential, arising when only the screening potential due to the valence charge is subtracted from the PP. With the introduction of the core correction, a smoothed core charge is added to the valence charge density as well. We chose the radius at which this correction is made to be slightly larger than the radius where the AE core and valence charge densities cross. The optimized PP parameters are given in Table I for different orbitals and compared with the developers' parameters.

The valence electrons were described by localized pseudoatomic orbitals (PAOs) with a double- $\zeta$  singly polarized (DZP) basis set. We experimented with a variety of LCAO basis sets and found that for both the graphite and SWCNT, the DZP produced high-quality results. In Fig. 1, we illustrate the convergence of the total electronic energy as a function of the number of orbitals for a (4,4) SWCNT. In switching from a single- $\zeta$ , singly polarized basis set (SZP) to DZP, the difference in binding energy was roughly 15 eV, whereas in switching from the DZP to triple- $\zeta$  singly and doubly polarized basis sets (TZP and TZDP, respectively), the energy differentials were less than 1 eV. DZP wins easily in a simple consideration of accuracy vs computational efficiency

The confinement of the atomic orbitals invariably leads to a rising of the energy levels, and we account for this by



FIG. 1. LCAO basis set convergence test performed for a (4,4) SWCNT. From a cost-benefit perspective, DZP produces the most accurate results. The labels stand for single (s), double (d), triple (t),  $\zeta$  (z), and polarized (p) orbitals.

choosing an energy shift for PAO (50 meV) that minimizes the total energy for a graphene sheet and corresponds to cutoff radii of 5.1 and 6.25 a.u., respectively, for the *s* and *p* orbitals. The convergence of the results in the real-space mesh size was investigated and we found that, in most cases, a plane-wave mesh cutoff of nearly 200 Ry produced satisfactory results.

#### A. Electronic spectra

SIESTA calculates the eigenvalue energies at each k point, so while increasing the number of k-points increases considerably the computational cost, it is necessary for acceptable convergence of electronic energies. The global structure of the electronic bands was not greatly affected by adjusting the number of k points. However, the converged bandwidth was approximately 1 eV higher than that obtained using a single k point for both the graphite and nanotube calculations. It was also essential to use many k points in order to obtain a detailed density of states (DOS). For graphite, it was found that a k grid cutoff of 25 Å, corresponding to 3465 k points, was necessary to converge the DOS. For the (10,0) SWCNT, using 900 k points resulted in a converged DOS.

In order to calculate the electronic band structures, SIESTA creates a supercell based on the user-specified unit cell. However, phonon calculations require that the user specify the spatial coordinates of every atom. Graphite coordinates were initially created by the SIESTA utility package VIBRA, while the nanotube coordinates were created from a program supplied in Ref. 1. Supercell coordinates were then input into SIESTA, where a molecular relaxation for graphene was initiated. This was done so that a more accurate ground-state configuration could be used in the subsequent phonon calculations. The GGA method was used for the relaxation, with the maximum force tolerance set at 0.04 eV/Å and the maximum atomic displacement set at 0.02 bohr. The same planewave mesh cutoff was used in the relaxation and phonon calculations, as were the cutoff radii. The number of iterations required to relax the system varied between the PP sets,



FIG. 2. Electronic energy dispersion relations for a graphene sheet using (a) the SIESTA developers' PP parameters and (b) this work. Troullier-Martin PP and GGA DFT flavor are employed in both cases. The mesh cutoff was 200 Ry, with 243 k points and a 50 meV PAO energy shift.

in the range from 1 to 20 cycles. Adjusting the number of k—points used in the relaxation had an insignificant effect. For the graphite, a k—grid cutoff of 15 Å adjusted the atomic positions by 0.01 bohr only, with respect to using a single k point. In our final analysis, we chose a 10 Å k grid cutoff. This, however, meant that different numbers of k points would be employed for each SWCNT.

#### 1. Graphene

In Fig. 2, we compare the graphene electronic dispersion energies when using the developers' PP parameters<sup>25</sup> and our optimized values for the core cutoff and core correction radii. The mesh cutoff was kept at 200 Ry, with 243 k points and a PAO energy shift of 50 meV. At the k=0 ( $\Gamma$ ) point of the first Brillouin zone, the so-called valence bandwidth of graphite—the bottom of the  $\sigma$  band—is 20.23 eV, compared with the experimental photoelectron momentum spectroscopy in graphite of 22.00 eV (Ref. 26); a pure LDA calculation yields a value of 19.6 eV.<sup>27</sup> The  $\pi$  valence bands exhibit strong dispersion and avoided crossings with the excited  $\sigma$ valence band. The bottom of the  $\pi$  band and the top of the



FIG. 3. Electronic density of states for a graphene sheet using the (a) SIESTA developers' PP parameters and (b) this work. A total of 3465 k points were employed.

first excited  $\sigma$  bands at the  $\Gamma$  point are, respectively, at -6.5 and -3.2 eV, compared with the experimental values of -6.6 and -5.5 eV.<sup>28</sup> It has been suggested that LDA results for the bandwidth in graphite are generally narrower than those obtained by including many-body effects, such as the exchange and correlation or self-energy terms.<sup>26</sup> As with most other studies of the graphite band structure, our results are for a 2D graphite monolayer, as the weak van der Waals interaction along the direction perpendicular to the graphite plane has little effect on the 2D energy structure.

Figure 3 presents calculations of the DOS for a graphene sheet using the developers' and optimized PP parameters. A large number of points in the Brillouin zone is needed to obtain converged results. The DOS shown here have been sampled with a 0.5 eV Gaussian filter. The DOS with the optimized PP parameters differs from that with the developers' parameters in the region of the step, near -20 eV, which is evidence for the nondispersive behavior of several electronic bands.

#### 2. SWCNT

DFT calculations of the (6,6) armchair SWCNT using the PP parametrized according to the developers' and optimized



FIG. 4. Electronic energy dispersion relations for an armchair (6,6) SWCNT using the (a) SIESTA developers' PP parameters and (b) this work. Five k points were employed and the mesh cutoff was at 200 Ry.

values produced nearly identical results for the valence bands in Fig. 4, but there are substantial differences between the upper conduction bands, where the results based on our PP parameters show more bands than are visible in Fig. 4(a). A similar conclusion can be drawn by comparing with a recent calculation of the (6,6) SWCNT band structure.<sup>29</sup> The two bands near the Fermi energy cross at  $\frac{2\pi}{3a}$ , where  $a=\sqrt{3}a_{cc}$  is the lattice constant for the graphene sheet from which the SWCNT is rolled and  $a_{cc} = 1.42$  Å is the carbon-carbon bond length. The X point corresponds to  $k = \pi/a$ . The crossing near the Fermi energy, of course, indicates that the (6,6) SWCNT is of the metallic variety. The supercell is generated from a single ring, the primitive unit cell of the system, which contains N=4n carbon atoms, where n represents an (n,n) armchair SWCNT. The electronic dispersion energies for a (10,0) zigzag SWCNT, using the optimized PP parameters, are shown in Fig. 5. The valence and conduction bands near the Fermi energy are repelled, illustrating the semiconducting nature of this SWCNT.



FIG. 5. Electronic energy dispersion curves for the zigzag (10,0) SWCNT using the optimized PP parameters.

The electronic densities of states for the (10,0) zigzag semiconducting SWCNT using the optimized PP are presented in Fig. 6. The density of states is zero at the Fermi energy, as would be expected for a semiconducting SWCNT. The density of states again has been sampled with a 0.5 eV Gaussian filter. The agreement between our calculations, in comparing the valence and conduction band peak positions and relative heights with the scanning tunneling microscope measurements of Odom *et al.*,<sup>30</sup> shown in Fig. 6(a), is encouraging. The prominent peaks refer to allowed electronic band transitions, whereas the small wiggles, which persist even after the Gaussian averaging, are the result of finite sampling in the Brillouin zone. As more *k* points are included, more smoothened DOS curves result.

### **B.** Phonon dispersion spectra

In Fig. 7, we present a comparison of calculations using the developers' and optimized PP parameters for the vibrational dispersion modes of graphene. We use a parallelogram-shaped supercell containing 98 atoms  $(3 \times 3)$  $\times 0$ , i. e., with two-atom unit cell in the center, three additional unit cells are added in each axial planar direction, resulting in a  $7 \times 7$  array of unit cells) with a saturated planewave cutoff of 400 Ry. Relaxing the atomic coordinates did not yield significant improvement of the phonon dispersion in graphite. We find reasonably good agreement with previous calculations<sup>31,32</sup> and experimental results.<sup>33</sup> For example, phonon frequencies at the  $\Gamma$  points, along the  $(\Gamma - M)$  and  $(\Gamma - K)$  directions, have been measured using inelastic x-ray spectroscopy of the phonon modes, respectively, at 1583 and  $1577 \text{ cm}^{-1}$ , whereas our calculations yield  $1627 \text{ cm}^{-1}$ . At the M point, the measured frequencies for the transverse- (TO) and longitudinal-optical (LO) modes are 1390 and  $1323 \text{ cm}^{-1}$ , while our calculations in Fig. 7(b) give 1448 and 1379 cm<sup>-1</sup>, respectively. The gap between the TO and LO modes at the K point is about 100  $cm^{-1}$  in our calculation, whereas the recent experimental value is 70 cm<sup>-1</sup>, and other



FIG. 6. Electronic density of states for the (10,0) zigzag SWCNT using the optimized PP parameters in (b) with 900 k points. The mesh cutoff was kept at 400 Ry and the PAO energy shift was 50 meV. The experimental observation of DOS, from Ref. 30, is also shown in (a).

calculations have reported 80 cm<sup>-1</sup> (Ref. 33) and 140 cm<sup>-1</sup> (Ref. 31). The acoustical modes, out of plane, transverse, and optical, starting at the  $\Gamma$  point are all well reproduced.

### C. Encapsulation in nanotube

We used the current DFT implementation with the optimized PP to calculate the electronic band structure for a pristine (10,10) nanotube and one filled with a potassium-iodide (KI) matrix [KI@(10,10)]. All calculations were done using three unit cells. In each supercell, linear chains of K and I atoms were placed according to their ion radii, 1.33 and 2.20 Å, respectively, in a (10,10) SWCNT cage. Altogether, each supercell contained 120 C, 4 K, and 4 I atoms. In the transverse plane, K and I atoms were separated by 4 Å and along the tube the atoms were placed 3.69 Å apart.<sup>34</sup> It was observed in high-resolution tunneling electron microscopy<sup>35</sup> that, in the lateral direction, the KI spacing was 3.5 Å and the tetragonal expansion of the lattice along the SWCNT axis was 4 Å. The plane-wave cutoff radius was set at 200 Ry with 20 k points and a PAO energy shift of 50 meV. The planar lattice parameters, which in the calculation corre-



FIG. 7. Phonon dispersion modes in graphene. A total of 98 atoms, arranged in  $3 \times 3 \times 0$   $(N_x, N_y, N_z)$ , were used, where  $N_x, N_y, N_z$  refer to the number of atoms on each side of the central carbon atom in the unit cell.

spond to the distance between neighboring tubes, were chosen to be large enough to prevent intertube interactions. The PP cutoff radii for K and I atoms were taken from Ref. 36.

The results are shown in Fig. 8. The naked (10,10) SWCNT spectrum is modified from the single-cell results due to the fact that now the spectrum is triply folded and the Fermi crossing occurs at  $k = \frac{2\pi}{9a}$ . The encapsulation slightly modifies the behavior of the conduction bands but dramatically alters the valence bands below the Fermi level. Many more valence bands appear in the KI@(10,10) SWCNT. The first introduction of extra nearly dispersion-free valence bands occurs near -1 eV due to the presence of the I(5p<sub>3/2</sub>) orbital interacting with the carbon orbitals. The next crowding of bands, also dispersion-free, occurs near -14 eV due to the presence of the K(3p) orbital (not shown).

The SWCNT charge density in the absence (presence) of encapsulated KI matrix is shown in Fig. 9(a) [Fig. 9(b)]. The I atom is shown in the plane and the K atom is above the plane. The carbon bonds are also shown. One observes a modification of the carbon charge density when the KI matrix is introduced.



FIG. 8. Naked (10,10) and filled KI@(10,10) nanotubes. The results are shown for a three-ring supercell containing 120 C atoms in (a) and an additional 4 I and 4 K atoms in (b). The Fermi crossing is now at 1/3 the distance from the  $\Gamma$  point, at  $k = \frac{2\pi}{a_a}$ .

### **III. SUMMARY**

Using an order-*N* implementation of generalized-gradient density-functional method, we have generated total-energy-conserving pseudopotentials for the core electrons and calculated electronic and phonon dispersion energies for a graphite monolayer and a number of zigzag and armchair carbon nanotubes. Comparisons were made with previous calcula-



FIG. 9. (Color online) (10,10) SWCNT charge density in the absence of (top) and due to the presence of K and I ions. The I atom is in the plane and the K atom is above the plane. The charge density is modified.

tions and experiments, where available. We have also investigated the encapsulation of a (10,10) carbon nanotube with a KI molecular matrix and found modification of the valenceband structure due to the introduction of ionic K<sup>+</sup>I<sup>-</sup> bonds. Since encapsulation is a more preferred method of "doping" in nanotubes, due to air stability, we intend to continue the investigation of encapsulation of different molecules in SWCNT with an aim toward the manipulation and control of its electronic properties.

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